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between specimens of lead of different geographical origin, and (3) that the atomic weight of lead referred to silver as 107.880 is very nearly 207.20.

We are very greatly indebted to the Carnegie Institution of Washington for generous assistance in the pursuit of this investigation.<sup>3</sup>

<sup>1</sup> *Proc. Amer. Acad.*, **43**, 365 (1907); *J. Amer. Chem. Soc.*, **30**, 187; *Zeit. anorg. Chem.*, **57**, 174.

<sup>2</sup> See, Richards and Lambert, *J. Amer. Chem. Soc.*, **36**, 1329 (1914); M. Curie, *C. R. Paris Acad. Sci.*, **158**, 1676 (1914); Hönigschmid and St. Horowitz, *Ibid.*, **158**, 1796 (1914); Soddy and Hyman, *J. Amer. Chem. Soc.*, **105**, 1402 (1914).

<sup>3</sup> This work will be described in detail before long in *Proc. Amer. Acad. Arts Sci., Boston*, and in *J. Amer. Chem. Soc.*

## A REVISION OF THE ATOMIC WEIGHT OF PRASEODYMIUM

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Some years ago the atomic weight of neodymium was investigated in the Harvard Chemical Laboratory by the analysis of the chloride;<sup>1</sup> and the success met in obtaining pure material and in the method used, led us to investigate in a similar fashion the atomic weight of the twin element praseodymium. The International Committee upon Atomic Weights has chosen the value 140.6 for this constant, yet some of the recent investigations, notably those of Brauner, have yielded considerably higher results, in the neighborhood of 141.

Naturally, the first problem in the investigation was to prepare pure praseodymium salt. Through the great kindness of Dr. H. S. Miner of the Welsbach Light Company we were fortunate enough to secure as a starting point about 10 kg. of crude praseodymium ammonium nitrate, containing about 50% of the corresponding lanthanum and cerium salts as well as a small amount of neodymium. Since one of the most rapid and effective methods of freeing praseodymium salts from the closely related elements, lanthanum, cerium, neodymium, and samarium is the fractional crystallization of the double ammonium nitrate, we chose this method of purification. In this crystallization the bases separate in the order lanthanum, cerium, praseodymium, neodymium, samarium, and yttrium earths. The usual method of fractional crystallization was followed;<sup>2</sup> that is, the mother liquor of a less soluble fraction was used for dissolving the crystals of the next more soluble fraction. The crystallization proceeded with the occasional rejection of fairly large fractions, chiefly lanthanum and cerium, at the less soluble end of each series, and the rejection of much smaller fractions, partly neodymium, at the more

soluble end, until 174 series of crystallizations had been made. The number of fractions in each series rapidly increased to a fairly constant number between 20 and 25. In series 174 an examination of the absorption spectra of the more soluble fractions showed that the extreme fraction contained a very small quantity of neodymium, not more than 0.05%, and that samarium was absent. At this point the seventh fraction from the more soluble end, 3474, was removed for analysis, since it seemed likely that this fraction was as pure as any in the series, and the more soluble fractions were rejected. Fractional crystallization was then continued for 41 more series, without, however, rejecting any material at the more soluble end, although the least soluble fraction was occasionally discarded. The most soluble fraction of the 215th series, 4383, upon careful examination of the absorption spectrum, was still found to be free from neodymium, although it was found possible by the absorption spectrum to detect less than 0.05% of the latter element. This result indicates that the other fractions also were free from both neodymium and samarium. The least soluble fraction, 4368, was analyzed for cerium by precipitating the hydroxide and treatment with chlorine, and was found to contain 0.4%. The atomic weight of cerium is so nearly like that of praseodymium that even this proportion would lower the observed atomic weight of praseodymium less than 0.003 unit. Fraction 4371 was found to contain only 0.1% of cerium.

The quantitative examination of selected fractions of the last series was then undertaken. First, the double nitrate was converted into chloride. This was done by precipitating praseodymium oxalate, igniting the washed and dried product to oxide, dissolving the oxide in nitric acid, reprecipitating and igniting the oxalate, dissolving the oxide in hydrochloric acid in a quartz dish, and crystallizing the product from concentrated hydrochloric acid solution. The salt was then superficially dried in a vacuum desiccator.

In order to dry the salt for weighing, it was carefully dehydrated by efflorescence at gradually increasing temperatures in a current of dry hydrochloric acid gas. The salt was contained in a weighed platinum boat, and this was placed in a quartz tube forming part of a Richards 'bottling apparatus'.<sup>73</sup> When essentially all the water had been expelled the temperature was raised rapidly until the salt was fused. After the salt had been allowed to cool the hydrochloric acid was displaced by dry nitrogen and this in turn by dry air. Then the boat was transferred to the weighing bottle without exposure to moisture, and it was weighed.

Upon treating salt thus prepared with pure water, sometimes a very small proportion of insoluble matter is found. The proportion of this material depends upon the care with which the salt is first dehydrated

previous to fusion. Careful analysis of this material showed it to be praseodymium oxychloride. By exercising every precaution in the drying of the salt and by fusing the salt as rapidly as possible, formation of the oxychloride can either be avoided completely or kept within a limit so small as to produce no important effect upon the final result. These precautions were taken in drying all the specimens of chloride.

The solution of the praseodymium chloride was precipitated in dilute solution with a solution of a weighed amount of the purest silver very nearly equivalent to the chloride. By examination of the mother-liquor with a nephelometer it was determined whether the amount of silver used was exactly equivalent to the chloride, and an initial deficiency or excess was made up with very dilute standard solutions. Finally the silver chloride was collected and weighed. Corrections were applied for moisture retained by the silver chloride and for the silver chloride dissolved in the washings.

The following table gives a comparison of the results obtained with the various fractions of the last series, as well as with the one selected from series 174, Fraction 3474. Of the others, Fraction 4383 is the most 4368 the least soluble. As a rule 5 to 6 gram portions of the chloride were used. Vacuum corrections were applied to the apparent weights of praseodymium chloride, silver, and silver chloride.

It is apparent that the variations among the different fractions are chiefly fortuitous; for the extreme fractions examined show a difference which is hardly beyond the experimental error of analysis. The atomic weight of praseodymium seems to be very nearly 140.92, if silver is taken

THE ATOMIC WEIGHT OF PRASEODYMIUM

Ag = 107.880

Cl = 35.457

FRACTION	PrCl <sub>3</sub> : 3Ag	PrCl <sub>3</sub> : 3AgCl	AVERAGE VALUES
3474		140.913	
3474		140.939	
3474	140.943	140.923	
3474	140.924		
3474	140.914	140.941	
Average . . . . .	140.927	140.929	140.928
4383	140.910	140.909	
4383	140.914	140.902	
Average . . . . .	140.912	140.906	140.909
4381	140.908	140.937	
4381	140.920		
4381	140.915	140.925	
4381	140.921		

## THE ATOMIC WEIGHT OF PRASEODYMIUM—Continued

FRACTION	PrCl <sub>3</sub> : 3Ag	PrCl <sub>3</sub> : 3AgCl	AVERAGE VALUES
Average . . . . .	140.916	140.931	140.921
4379	140.910	140.913	
4379	140.915	140.928	
Average . . . . .	140.913	140.921	140.917
4377	140.917		
4377	140.917	140.951	
Average . . . . .	140.917		140.928
4374	140.916	140.965	
4374	140.916	140.943	
4374	140.959	140.952	
4374	140.926	140.911	
4374	140.911	140.916	
4374	140.911		
Average . . . . .	140.923	140.937	140.930
4371	140.915	140.926	
4371	140.922	140.924	
Average . . . . .	140.919	140.925	140.923*
4368	140.916	140.935	
4368	140.922	140.919	
Average . . . . .	140.919	140.927	140.925†
Final Average . . . . .			140.923
Average of all Individual Analyses . . . . .			140.924

\* Increased by + 0.001 units to correct for cerium-content.

† Increased by + 0.002 units to correct for cerium-content.

at 107.880. This result is not far from the value obtained by Brauner in both his researches, but is over three-tenths of a unit higher than the choice of the International Committee on Atomic Weights.

We are indebted particularly to the Carnegie Institution of Washington for very generous assistance in carrying out this investigation,<sup>4</sup> as well as to Dr. H. S. Miner of the Welsbach Light Company for the praseodymium material.

<sup>1</sup> Baxter and Chapin, *Proc. Amer. Acad.*, **46**, 213 (1911).

<sup>2</sup> The crystallization was begun by Mr. W. H. Whitcomb, continued by Messrs. B. W. Grimes and C. C. Wallace, and completed by O. J. Stewart.

<sup>3</sup> Richards, *Proc. Amer. Acad.*, **32**, 59 (1896).

<sup>4</sup> This work will be described in detail before long in *Proc. Amer. Acad. Arts Sci., Boston*, and in *J. Amer. Chem. Soc.*